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(54) Title of the Invention: **Dry Etching Method**

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SPECIFICATION

1. Title of the Invention

Dry Etching Method

2. Claims

1. A dry etching method in which a gas containing a halogen and a gas for forming a thin film on the surface of a treatment material are alternately introduced into a vacuum chamber, and a thin film is formed on the surface of the treatment material by performing a chemical treatment in the introduced gas or an excited gas plasma, wherein said dry etching method is characterized in that the gas for forming a thin film comprises one or more members of the group consisting of hydrocarbon-based gas, oxygen compound-based gas, and silicon compound-based gas.

2. The dry etching method according to Claim 1, characterized in that the hydrocarbon-based gas is selected from the group consisting of CCl_4 (tetrachloromethane), CH_3F (fluoromethane), CH_2F_2 (difluoromethane), C_2F_6 (hexafluoroethane), C_3F_8 (perfluoropropane), C_4F_9 (perfluorobutylene), CH_4 (methane), C_2H_4 (ethylene), $CClF_3$ (chlorotrifluoromethane), CCl_2F_2 (dichlorodifluoromethane), $C_2Cl_3F_3$ (trichlorotrifluoroethane), $C_2Cl_2F_4$ (dichlorotetrafluoroethane), and C_2ClF_5

(chloropentafluoroethane), the oxygen compound-based gas is either O_2 (oxygen) or H_2O (water vapor), and the silicon compound-based gas is selected from the group consisting of SiH_4 (silane), Si_2H_6 (disilane), SiH_2Cl_2 (dichlorosilane), $SiHCl_3$ (trichlorosilane), $SiCl_4$ (tetrachlorosilane), and SiF_4 (tetrafluoroethane).

3. Detailed Description of the Invention

Field of Industrial Utilization

The present invention relates to a dry etching method, and more particularly relates to a dry etching method that is favorable in terms of preventing side etching when a thin film is formed on the surface of a material.

Prior Art

One conventional dry etching method aimed at improving dimensional precision involved simultaneously introducing two or more types of gas into a vacuum chamber, as discussed in Solid State Technology (1984, pp. 235-242). Specifically, the etching shape was controlled, and more particularly, side etching was suppressed, in the formation of a gate composed of a two-layer film comprising tungsten silicide and polysilicon (such a gate is also called a polycide gate) by dry etching in a plasma of a mixture of two types of gas comprising SF_6 (sulfur hexafluoride) and C_2ClF_5 (a type of fluorochloro-substituted hydrocarbon, whose chemical name is chloropentafluoroethane, and which also goes by the trade name of Freon 115). Tungsten silicide and polysilicon can both be etched in a plasma of SF_6 gas alone, but a drawback to using a single gas was that an extremely large amount of side etching occurred. Consequently, in the example cited above, C_2ClF_5 was included in the mixed gas in order to suppress this side etching, and the amount of side etching of the tungsten silicide and polysilicon was reduced by optimizing the mixture ratio of the SF_6 and C_2ClF_5. The reason the amount of side etching is reduced in this case is believed to be that hydrocarbon polymers tend to be produced in a C_2ClF_5 plasma, and

these polymers adhere to the side walls of the [etching] pattern, where they serve as side wall protection films that prevent side etching.

Problems Which the Invention is Intended to Solve

Unfortunately, the following problems were encountered in etching with a gas mixture as discussed above. First, since plasma reactions with two types of gas proceed simultaneously, the reaction is complex and difficult to control. Optimizing the etching conditions therefore takes considerable time. Second, when reactions with two different types of gas are conducted alternately, this often leads to problems such as a lower etching rate or selectivity than when a single etching gas is used.

It is an object of the present invention to solve the above problems and provide a high-precision dry etching method with which side etching can be reduced.

Means Used to Solve the Above-Mentioned Problems

The stated object is achieved by a dry etching method in which a hydrocarbon-based gas, an oxygen compound-based gas, or a silicon compound-based gas, or a mixture of two or more of these, is used to form a thin film on the surface of a treatment material, this gas and a gas containing a halogen are supplied alternately into a vacuum chamber, and the surface of the treatment material is chemically treated in a plasma of each gas.

Specifically, an etching gas such as SF_6 and a polymer film-forming gas such as CCl_4 (tetrachloromethane) are alternately supplied into a vacuum chamber and converted into a plasma, so that etching with an SF_6 plasma is alternated with the formation of a polymer film on the surface of the treatment material with a CCl_4 plasma.

It is preferable for the pump exhaust rate to be high in order for the gas replacement to be carried out in a shorter time and more efficiently. Naturally, even if the pump exhaust rate is low, it is still possible to employ a method in which when it is time for gas replacement, the plasma discharge is temporarily halted, the gas is replaced, and discharge is then started again, but the problem with this is that the etching takes

much longer. As for the etching apparatus, it is better to use a microwave excitation plasma etching apparatus with a low gas treatment pressure of about 10^{-4} to 10^{-3} Torr, rather than an RF (high frequency) excitation etching apparatus with a treatment gas pressure of anywhere from a few dozen Torr to a few hundred Torr. The reason for this is that plasma discharge and etching can be carried out stably at a lower gas pressure, and gas replacement can be completed in a short time of no more than a few seconds.

Operation of the Invention

The above method allows, for the following reason, anisotropic etching to be performed with very little side etching. A carbon-based polymer film is formed on the surface of a treatment material exposed to a plasma of CCl_4. Etching commences when the gas is then changed from CCl_4 to SF_6, and the polymer film is removed from just the horizontal part of the treatment material irradiated with ions, and the etching proceeds in the depth direction. Meanwhile, since the side walls of the pattern are not irradiated with as many ions, the deposited polymer film remains throughout the etching cycle and serves as a side wall protective film that prevents the side etching of the pattern side walls. The polymer deposition formation step and the etching step are repeated numerous times for a short time each, which affords anisotropic etching with little side etching.

Examples

Examples of the present invention will now be described.

Example 1

The surface of a silicon (Si) substrate was etched with a gas chopping method in which SF_6 was used for the etching gas and CCl_4 was used for forming a pattern side wall protective film, and these gases were supplied alternately by time division. The etching apparatus was the microwave plasma etching apparatus shown in Fig. 1. In Fig. 1, 1 is a microwave generator, 2 is a microwave generator power supply, 3 is a waveguide, 4 is a discharge tube, 5 is an electromagnet, 6 is a vacuum chamber, 7 is a pipe, 8 is a gas flux

regulator valve, 9 is a gas cylinder, 10 is a sample, 11 is a sample holder, 12 is a permanent magnet that forms a mirror magnetic field along with the electromagnet 5, and 13 is a controller. The gas flux was 10 to 20 cc/min and the discharge pressure was 1×10^{-3} to 3×10^{-3} Torr. The SF_6 and CCl_4 were alternately supplied to the treatment chamber in 10-second intervals, a plasma was generated, the silicon was etched with the SF_6 plasma, a carbon compound film was deposited onto the silicon surface by the CCl_4 plasma, and this cycle was repeated over and over. In the SF_6 step, an RF bias was applied to the sample for 5 seconds in order to remove the deposited film on the horizontal portions in a shorter time.

Fig. 2 shows the side etching suppression effect. Compared to etching with just SF_6, there was far less side etching with the gas chopping method in which SF_6 and CCl_4 were supplied alternately. It was confirmed by XPS (X-ray Photoelectron Spectroscopy) that a film whose main components were carbon and chlorine had been formed on the silicon surface in the CCl_4 plasma. This deposited film protected the silicon pattern side walls during the etching, reducing the amount of side etching to less than one-fifth, as shown in Fig. 2.

It was found that a carbon compound-based protective film can be formed using not only CCl_4, but also CH_3F (fluoromethane), CH_2F_2 (difluoromethane), C_2F_6 (hexafluoroethane), C_3F_8 (perfluoropropane), C_4F_9 (perfluorobutylene), CH_4 (methane), C_2H_4 (ethylene), $CClF_3$ (chlorotrifluoromethane), CCl_2F_2 (dichlorodifluoromethane), $C_2Cl_3F_3$ (trichlorotrifluoroethane), $C_2Cl_2F_4$ (dichlorotetrafluoroethane), and C_2ClF_5 (chloropentafluoroethane).

Example 2

A gas chopping process was carried out using O_2 (oxygen) instead of the CCl_4 used in Example 1. In this case, a silicon oxide film served as the side wall protective film since the silicon pattern side walls were oxidized in the O_2 plasma, and this reduced the amount of side etching to 0.05 μm or less. It was found that an oxygen compound-based protective film can be formed using H_2O (water vapor) as well as O_2.

Example 3

A gas chopping process was carried out using a mixture of SiF_4 (tetrafluorosilane) and O_2 instead of the CCl_4 used in Example 1. The treated material was tungsten. A film of silicon oxide was formed on the tungsten surface by the mixed gas plasma of SiF_4 and O_2. It was found that the silicon oxide film acted as a protective film that reduced the side etching of the tungsten. In addition to SiF_4, it was found that a silicon compound-based protective film could also be formed using SiH_4 (silane), Si_2H_6 (disilane), SiH_2Cl_2 (dichlorosilane), $SiHCl_3$ (trichlorosilane), or $SiCl_4$ (tetrachlorosilane).

The above Examples 1 to 3 involved the use of a gas chopping process in which a gas for forming a protective film and an etching gas were alternately supplied, but a protective film can also be formed when the supply periods of the protective film forming gas and the etching gas overlap partially, or in other words, when there is a period in which two different types of gas are admixed at the same time. Still, the efficiency of film formation in this case was lower than with a gas chopping method, and characteristics such as etching rate and etching selectivity were also markedly inferior.

The dry etching apparatus used in Examples 1 to 3 was a microwave plasma etching apparatus, but the side etching suppression effect in a gas chopping method will be the same with an RF discharge reactive plasma etching apparatus. In the case of an RF discharge type of apparatus, however, the treatment gas pressure is high (several dozen to several hundred Torr), so gas replacement takes longer. It is necessary to use a method in which the discharge is temporarily halted at the time of gas replacement.

In Example 1, the silicon can also be etched with CCl_4 alone. In this case, depending on the conditions under which the CCl_4 plasma is produced, there are situations in which the silicon is etched, and situations in which a carbon compound is deposited on the silicon surface. For instance, [the silicon] is etched at a gas pressure of 0.5×10^{-4} Torr, but a film is deposited at 5×10^{-3} Torr. Anisotropic etching can be performed while etching is alternated with side wall protective film formation by switching back and forth between the above two conditions in time division. In this case, though, the silicon etching rate drops to about one-tenth that when SF_6 is used as the etching gas, which is a problem in terms of throughput. The same effect as with the

above switching of the gas pressure can be obtained with a method in which the bias applied to the sample is switched between large and small in time division.

Furthermore, it was found that when CF_4 (carbon tetrafluoride) was used as the film forming gas in aluminum (Al) dry etching with BCl_3 (boron trichloride), the [resulting] aluminum fluoride served as a protective film that suppressed side etching.

Effect of the Invention

As described above, the present invention allows anisotropy to be easily achieved in dry etching, improves micro-working precision, and contributes to higher integration for LSI (Large Scale Integrated) or VLSI circuits. It was confirmed that side etching can be reduced to 0.05 μm or less in the etching of silicon and tungsten when the present invention is employed.

4. **Brief Description of the Drawings**

Fig. 1 is a diagram illustrating an example of the etching apparatus used in the implementation of the method of the present invention; and

Fig. 2 is a diagram illustrating the effect of the present invention, shown by the amount of side etching.

Key:

1 … microwave generator	3 … waveguide
4 … discharge tube	5 … electromagnet
6 … vacuum chamber	7 … pipe
8 … gas flux regulator valve	9 … gas cylinder
10 … sample	11 … sample holder
12 … permanent magnet	

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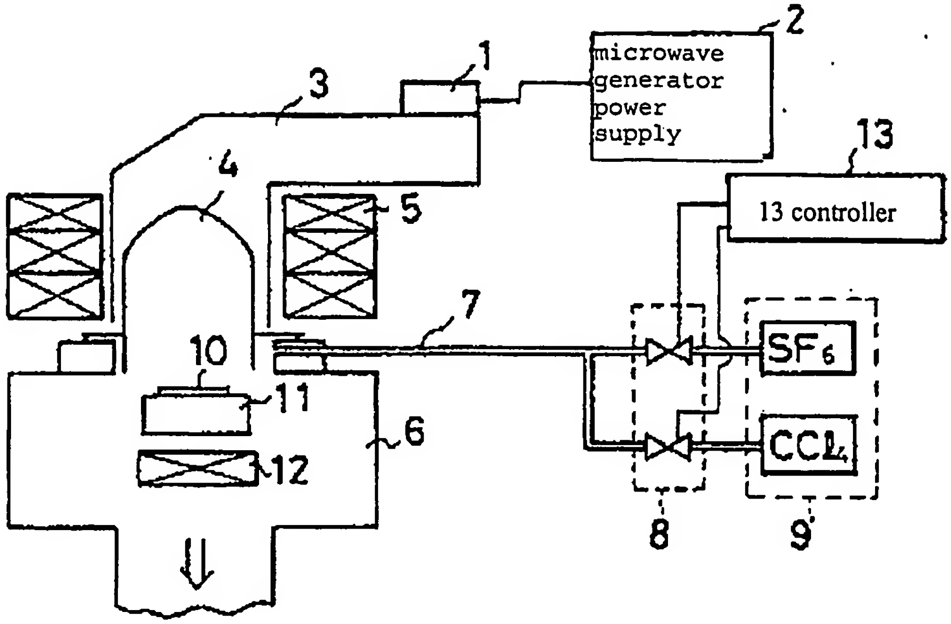
Fig. 1



1 … microwave generator
3 … waveguide
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Fig. 2